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Lubricant-coated metal sheet having improved forming properties

The invention relates to a lubricant-coated metal sheet or a section thereof having improved forming properties, whereby the lubricant is in particular a corrosion protection oil, pre-lube and/or dry lube. The invention further relates to a method for the manufacture of such a metal sheet or metal sheet section, as well as to its use for the manufacture of metal bodies by forming, in particular by deep-drawing.

In the manufacture of metal sheets, such as steel sheets, it is common for these to be provided with a temporary corrosion protection for storage and transport immediately after the manufacturing or coating process and before delivery to the metal-processing industry. This is usually effected by applying a corrosion-inhibiting lubricant directly before the coiling of the sheet, such as a corrosion protection oil, a pre-lube or a dry-lube. If the metal sheet is destined for further processing by forming such as deep-drawing, the lubricants used can contain, in addition to corrosion-inhibiting substances, other ancillary substances, especially matched to the individual forming process, which improve the tribological properties of the sheet during the forming process. Metal sheets coated in this way are encountered, for example, in the automobile industry in the manufacture of bodywork made of metal sheets by deep-drawing.

With the use of lubricants for temporary corrosion protection and for improving the forming properties, it must be particularly borne in mind that these are to be easily and completely removable after the forming process.

From EP 0 489 105 B1 a method is known for the cold deep-drawing of metal sheets, in which the sheet which is to be deep-drawn and/or the deep-drawing tool are treated with an aqueous solution of an inorganic alkali phosphate and are then deep-drawn in the presence of a deep-drawing oil. The salt which is deposited on the sheet forms a soap under the pressure and temperature conditions of the deep-drawing process as a result of the reaction with the deep-drawing oil, which has the effect of reducing the friction coefficient. A disadvantage of the method is that the alkali phosphate used and the soap which is formed cannot be entirely removed from the sheet, free of any residue, after the deep-drawing.

From CH 441 594 a lubricant composition is further known for the cold-forming of metals without the removal of material, which contains a finely dispersed water-soluble inorganic salt for the improvement of the tribological properties, such as Borax. A disadvantage with this lubricant composition is that its lubrication capacity is not constant, since the salt is not distributed uniformly over the surface, which interferes with the deep-drawing process.

With the production of single-sided electrolytically galvanized fine sheet, very thin phosphating or borax passivation with a coating weight of approx. 10 mg/m2 has proved advantageous in respect of tribological properties. Both products can be applied in the existing flushing

baths of the galvanizing lines, but they have the disadvantage that they may impair the phosphating process in the automobile production plant.

The use of prelubes takes account of the idea of influencing the tribological properties of steel strip directly on the surface of the steel. Prelubes contain drawing aids which are introduced into the oil coating, which is about 1 μm thick. Only the direct steel-tool interface is tribologically active, in the range of a few nanometres.

Finally, the principle is generally known of carrying out a surface treatment of the deep-drawn sheet in order to improve the tribological properties. In particular, chemical processes for the surface treatment are known, such as phosphating, by means of which the friction coefficient between the sheet and the tool is reduced, and the forming of the sheet section is thereby facilitated. Such a treatment, however, is expensive and cannot be applied to all deep-drawn sheets.

It is an object of the present invention to provide a lubricant-coated metal sheet for the manufacture of metal bodies by forming, with improved tribological properties. The metal sheet should be easy to clean after the forming process and without any residues remaining. Finally, the manufacture of the lubricant-coated metal sheet should be capable of being carried out easily and without high investment expenditure in existing manufacturing facilities.

This object is achieved according to the invention by a metal sheet or a metal sheet section comprising a coating

of lubricant, in particular a corrosion protection oil, pre-lube and/or dry-lube, whereby the metal sheet or the metal sheet section comprises a layer which is formed by the application of a solution containing an organic phosphoric acid ester onto the metallic surface of the sheet.

Surprisingly, it has been found that the lubricant-coated metal sheets according to the invention have excellent tribological properties as a consequence of their layer formed by the phosphoric acid ester. By contrast with lubricant-coated metal sheets without such a layer, the metal sheets according to the invention have a reduced friction coefficient. Finally, the metal sheets according to the invention can be easily cleaned after the forming process by existing degreasing systems, whereby both the layer containing the lubricant as well as the layer formed by the phosphoric acid ester can be removed from the surface of the sheet with no problem at all and without leaving any residue.

The metal sheets which are capable of being used according to the invention can be any desired metal sheets from which metal bodies can be manufactured by forming, in particular by cold forming. Particularly suitable metal sheets are steel sheets. The metal sheets which can be used according to the invention can be coated or uncoated. As an uncoated metal sheet, for example, consideration can be given to uncoated fine sheet metal, in particular conti-annealed uncoated fine sheet metal. As a coated metal sheet, consideration can be given in particular to electrolytically coated sheet, as well as to hot-dip galvanized and galvanized sheets. The metal sheets

preferably have a thickness of 0.05 to 5 mm, and in particular from 0.5 to 1.5 mm.

The metal sheets and metal sheet sections according to the invention are coated with a lubricant which is intended to protect the sheets after manufacture, at least temporarily, against undesirable environmental influences, and in particular against corrosion manifestations. The choice of lubricant is not restricted; on the contrary, any substances containing grease or oil or the like, as well as dry lubricants such as graphite, come into consideration. The lubricants which can be used according to the invention preferably contain corrosion inhibitors. In addition, the lubricant can also contain further additives, in particular additives for improving the drawing properties of the sheets.

Such lubricants for the metalworking industry are in general known to the person skilled in the art, and are described, for example, in Nachtmann, *"Lubricants and lubrication in metalworking operations"*, Marcel Decker, New York, 1985, pages 81 to 105; Byers, *"Metalworking fluids"*, Marcel Decker, New York, 1994, pages 136 to 140, and Mortier, Orszulik, *"Chemistry and Technology of Lubricants"*, 2nd edition, Chapman & Hall, London, 1997, pages 253 to 260.

According to a preferred embodiment of the invention, a corrosion protection oil is used as the lubricant. Such corrosion protection oils are generally known to the person skilled in the art, and usually contain a basic oil with an aromate content < 10 % and a corrosion inhibitor such as, for example, calcium sulphonate. In addition, the corrosion protection oils can also contain anti-

oxidants for the prevention of oil aging, as well as thixotropy forming agents for reducing drip losses with oiled sheets.

According to a further preferred embodiment of the invention, a so-called "pre-lube" is used as a lubricant. Pre-lubes are corrosion protection oils with improved drawing properties, and as such are generally known to the person skilled in the art. The improvement of the drawing properties is achieved by the addition of further additives, e.g. of esters.

According to a further preferred embodiment of the invention, a so-called "dry lubricant" is used as a lubricant. Dry lubricants are thin films on wax and/or acrylate bases, with similar properties to pre-lubes, and as such as generally known to the person skilled in the art. In addition to this, dry lubricants also offer the possibility of manufacturing difficult drawing components in pressing plants without further additional lubrication. Drip losses from coated sheets are avoided entirely. Dry lubricants can be applied after smelting, for example by electrostatic means or by means of roll coaters.

According to the invention, a layer is formed on the metallic surface of the sheet, which can be obtained by the application of an organic phosphoric acid ester onto the metallic surface of the sheet.

Organic phosphoric acid esters which can be used according to the invention are, in particular, combinations of the general formula

$$X_{3-n}PO_4R_n$$

where X represents hydrogen, Na, K, $-NH_2$, $-NHR$, $-NR_2$, $-NH(R'-OH)$, $-N(R'-OH)_2$, or $-NR(R'-OH)$, R represents a straight-chain or branched alkyl group with 1 to 14 carbon atoms, in particular 1 to 8, R' is a straight-chain or branched alkyl group with 1 to 14 carbon atoms, in particular 1 to 8, whereby one or more hydrogen atoms in R and R' can be substituted by a polymer or oligomer group -Y-R, where Y represents $(CH_2-CH_2-O-)_m$ or $(CH_2-CH(CH_3)-O-)_m$ with m = 1 to infinity, and, in particular, m = 1 to 10, R and R' can in each case be equal or different, and n is a number from 0 to 3, with the proviso that n is not 0 if X stands exclusively for hydrogen.

Particularly good results are achieved if, as an organic phosphoric acid ester, a combination of the formula given above is used, with X = H, R = C_4H_9 and n = 1 or 2. Particularly preferred, in addition, is an equimolar mixture of $(C_4H_9-O)PO(OH)_2$ and $(OH)PO(O-C_4H_9)_2$.

According to a preferred embodiment of the invention, the layer formed by the phosphoric acid ester contains, as further components, a water-soluble organic sulphur compound and/or an organic molybdenum compound.

Suitable organic sulphur compounds according to the invention are, in particular, thiadiazoles, dithiocarbamates, and/or dithiopropionates, as well as their salts and derivatives.

Especially suitable organic sulphur compounds are, for example, sodium-2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, as well as salts and derivatives thereof, sodium dimethyl dithiocarbamate, potassium

dimethyl dithiocarbamate, and/or monoethanol amine dithiopropionate.

Organic molybdenum compounds which are suitable according to the invention can be obtained, for example, by the conversion of molybdenum trioxide and/or molybdeneic acid with an amine and/or alkanolamine.

According to a further preferred embodiment of the invention, the layer containing the phosphoric acid ester contains, as a further component, at least one inorganic compound from the group consisting of polyphosphates, borates, molybdates, and wolframates.

Inorganic compounds which are especially well-suited according to the invention are, for example, ammonium tripolyphosphate, sodium tetraborate, ammonium molybdate, sodium wolframate, potassium wolframate, and/or sodium wolframate.

Preferably, the organic phosphoric acid ester and any further components are applied onto the metal sheet in the form of an aqueous solution. After the application, the metal sheet is preferably dried.

The layer formed by phosphoric acid ester can be formed in any desired thicknesses. Preferably, however, this is a thin layer, in particular a coating in the nanometre range.

According to a further preferred embodiment of the invention, a layer containing a lubricant is formed directly onto a layer formed by phosphoric acid ester. The layer containing lubricant contains preferably a

corrosion protection oil, pre-lube, and/or dry-lube. Preferably, the layer containing lubricant contains a corrosion protection oil.

The layer containing lubricant can be formed in any desired thicknesses. Particularly good tribological properties can be achieved if the layer containing lubricant is formed in a thickness of 0.3 to 3.0 g/m^2, in particular 1 to 2 g/m^2.

It has proved to be particularly advantageous if the layer containing lubricant is matched to the layer containing phosphoric acid ester in such a way that it contains components which are contained in the layer containing phosphoric acid ester.

It has been found that a synergistic effect can be incurred by this measure, and the tribological properties of the sheet are improved still further.

It is therefore advantageous if the layer containing lubricant contains at least one organic phosphoric acid ester as defined above, in a quantity from 0.01 to 50 % by weight, and in particular 0.05 to 10 % by weight.

It is further advantageous if the layer containing lubricant contains an aqueous organic sulphur compound as defined above, in a quantity from 0.005 to 50 % by weight, in particular 0.01 to 30 % by weight, and/or an organic molybdenum compound as defined above in a quantity from 0.005 to 50 % by weight, in particular 0.01 to 30 % by weight.

Finally, it is advantageous if the layer containing lubricant contains an inorganic compound as defined above in a quantity from 0.005 to 50 % by weight, in particular 0.01 to 30 % by weight.

The invention further relates to a method for the manufacture of the metal sheet according to the invention or metal sheet sections, comprising the following steps:

- Application of a solution containing an organic phosphoric acid ester on the upper and/or lower side of the sheet, and

- Application of a lubricant onto the sheet coated in this way.

The application of the solution containing the organic phosphoric acid ester can be effected by any desired measures known to the person skilled in the art, such as immersion, spraying, brushing, or roll coating.

The procedure can be conveniently integrated into the existing work sequences in the manufacture of metal sheets. Accordingly, the application of the solution containing the phosphoric acid ester can be effected, for example, during the coating of the sheet in the flushing bath of a coating system or during the cooling of the sheet in the bath of a water cooling system. Preferably, the solution containing the phosphoric acid ester can be effected in the flushing bath of a coating system. The flushing bath in this situation is preferably arranged downstream as a single-step no-rinse post-treatment of the metallic coating process (e.g. electrolytic galvanizing). Within a production system, further production steps can

be arranged downstream of the flushing bath. In particular, the metal sheet can be dried after the flushing bath in a suitable drier and/or coated subsequently with a lubricant (e.g. by electrostatic oiling).

The solution containing phosphoric acid ester is preferably applied as an aqueous solution.

The solution contains the phosphoric acid ester preferably in a quantity from 0.1 to 15 % by weight, and in particular 3 to 8 % by weight.

The pH of the solution is adjusted preferably to a value of 6.5 to 11, in particular 7.5 to 9.5.

According to a preferred embodiment of the invention, the solution contains as further components, as described above, a water-soluble organic sulphur compound, in particular one of the compounds described heretofore, and/or an organic molybdenum compound, in particular one of the compounds described heretofore, and/or one of the inorganic compounds described heretofore. The water-soluble organic sulphur compound(s) and/or organic molybdenum compound(s) are contained in the solution preferably in a quantity from 1 to 50 % by weight, in particular from 5 to 25 % by weight, related to the quantity of phosphoric acid ester.

The inorganic compound(s) are contained in the solution in a quantity from 1 to 50 % by weight, in particular from 5 to 10 % by weight, related to the quantity of phosphoric acid ester.

Before the application of the lubricant it is advantageous for the sheet to be dried.

As a lubricant, preferably a corrosion protection oil, pre-lube and/or dry-lube is used, as described heretofore. Preferably, the lubricant is matched to the solution containing the phosphoric acid ester to such an extent that it contains components as described heretofore (e.g. organic phosphoric acid ester, water-soluble organic sulphur compound, organic molybdenum compound, and/or inorganic compound), which are also contained in the solution containing the phosphoric acid ester.

The lubricant is applied preferably in a quantity from 0.3 to 3 g/m^2, in particular 1 to 2 g/m^2.

The invention accordingly also comprises the use of a solution containing an organic phosphoric acid ester as described heretofore, for the treatment of metal surfaces.

The object of the invention is further an aqueous solution for the treatment of metal surfaces containing an organic phosphoric acid ester and a water-soluble organic sulphur compound and/or an organic molybdenum compound, all compounds as described heretofore, as well as a concentrate for the production of such a solution.

Finally, the use of the metal sheet or metal sheet section according to the invention comprises the manufacture of metal bodies by forming, in particular by deep-drawing.

The invention is described in greater detail hereinafter on the basis of an embodiment.

Electrolytically galvanized steel sheets of a thickness of 1 mm were treated by immersion in an aqueous solution of the composition described heretofore, dried, and then coated with 1.5 g/m^2 pre-lube. To match the drawing performance, the friction coefficient was then determined in the draw-bed test. As a reference for the friction coefficient, a sample of the electrolytically galvanized steel sheet was used, which was not treated with an aqueous solution. The friction coefficient of this reference sample was set at 100 %.

Example 1

An electrolytically galvanized steel sheet was treated with a 5 % solution of an equimolar phosphoric acid ester mixture of $(CH_3\text{-}O)PO(OH)_2$ and $(OH)PO(O\text{-}CH_3)_2$. The sheet was dried and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 88 %.

A reduction in the friction coefficient of 12 % was determined in comparison with the reference sample without pre-treatment.

Example 2

An electrolytically galvanized steel sheet was treated with a 5 % solution of an equimolar phosphoric acid ester mixture of $(C_4H_9\text{-}O)PO(OH)_2$ and $(OH)PO(O\text{-}C_4H_9)_2$. The sheet was dried and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 58 %.

A reduction in the friction coefficient of 42 % was determined in comparison with the reference sample without pre-treatment.

Example 3

An electrolytically galvanized steel sheet was treated with a 5 % solution of an equimolar phosphoric acid ester mixture of $(C_8H_{17}\text{-}O)PO(OH)_2$ and $(OH)PO(O\text{-}C_8H_{17})_2$. The sheet was dried and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 90 %.

A reduction in the friction coefficient of 10 % was determined in comparison with the reference sample without pre-treatment.

Example 4

An electrolytically galvanized steel sheet was treated with a 5 % solution of an equimolar phosphoric acid ester mixture of $(CH_3\text{-}[O\text{-}CH_2CH_2]_3\text{-}C_{12}H_{24}\text{-}O)PO(OH)_2$ and $(HO)PO(CH_3\text{-}[O\text{-}CH_2CH_2]_3\text{-}C_{12}H_{24}\text{-}O)_2$. The sheet was dried and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 92 %.

A reduction in the friction coefficient of 8 % was determined in comparison with the reference sample without pre-treatment.

Example 5

In this example, the deep-drawing working range of an electrolytically galvanized fine steel sheet manufactured in accordance with Example 2 was examined in relation to the reference sample without pre-treatment. The results of this examination are presented in Fig. 1.

The results show that the fine sheet coated according to the invention (Fig. 1b) has a perceptibly greater deep-drawing working range than the reference sample without pre-treatment (Fig. 1a).

Comparison example 1

An electrolytically galvanized steel sheet was treated with a 5 % sodium tetraborate solution, dried, and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 90 %.

A reduction in the friction coefficient of 10 % was determined in comparison with the reference sample without pre-treatment.

Comparison example 2

An electrolytically galvanized steel sheet was treated with a 5 % phosphoric acid ester solution, dried, and then coated with 1.5 g/m^2 pre-lube. The friction coefficient was 95 %.

A reduction in the friction coefficient of 5 % was determined in comparison with the reference sample without pre-treatment.

The results show that the metal sheets according to the invention which were treated with a phosphoric acid ester solution have perceptibly improved tribological properties in comparison with metal sheets which were not subjected to such treatment, as well as an enlarged deep-drawing working range. The metal sheets according to the invention were also capable of being cleaned easily and

entirely free of residue in a conventional degreasing system.